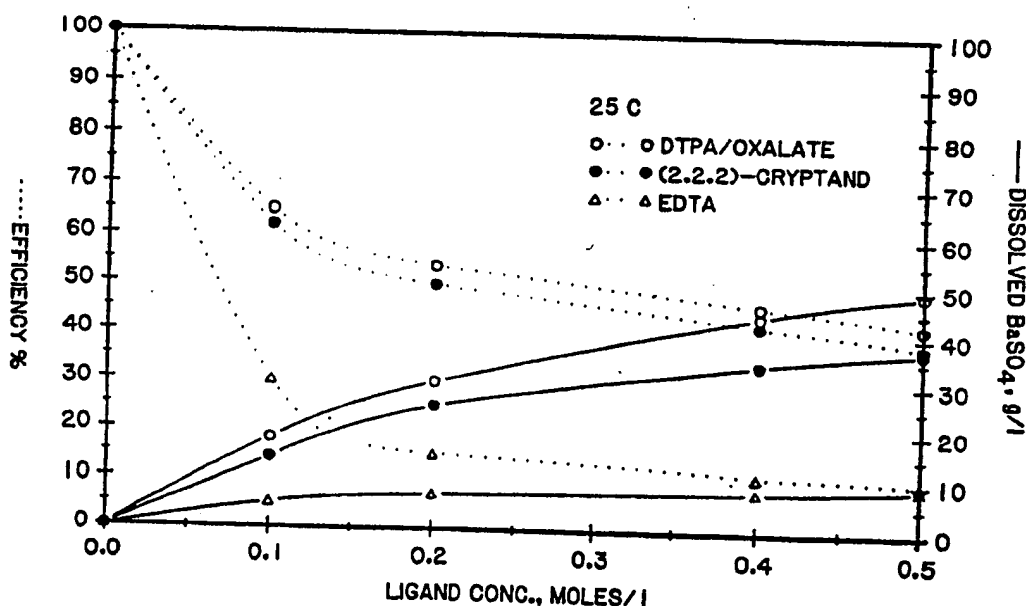




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|---|--|---|---|
| (51) International Patent Classification ⁵ : C02F 5/10, C23F 11/10 C23G 1/06 | | A1 | (11) International Publication Number: WO 90/11972 (43) International Publication Date: 18 October 1990 (18.10.90) |
| (21) International Application Number: PCT/US90/01774 (22) International Filing Date: 3 April 1990 (03.04.90) | | (74) Agents: ROBERTS, Peter, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US). | |
| (30) Priority data: 332,147 3 April 1989 (03.04.89) US 369,897 22 June 1989 (22.06.89) US 431,114 3 November 1989 (03.11.89) US 484,970 26 February 1990 (26.02.90) US 490,886 9 March 1990 (09.03.90) US not furnished 12 March 1990 (12.03.90) US | | (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent). | |
| (71) Applicant: MOBIL OIL CORPORATION [US/US]; 150 East 42nd Street, New York, NY 10017 (US). (72) Inventors: MORRIS, Richard, L. ; 202 North Venice, Duncanville, TX 75116 (US). PAUL, James, Mark ; 128 Williams, DeSoto, TX 75115 (US). | | Published With international search report. | |

(54) Title: SULFATE SCALE DISSOLUTION



(57) Abstract

Alkaline earth metal scales, especially barium sulfate scale deposits are removed from oilfield pipe and other tubular goods with a scale-removing composition comprising an aqueous alkaline solution having a pH of about 8 to about 14, preferably about 11 to 13, of a polyaminopolycarboxylic acid, preferably EDTA or DTPA and a catalyst or synergist comprising, in particular, oxalate, thiosulfate, nitriloacetate or monocarboxylic acid anions. When the scale-removing solution is contacted with a surface containing a scale deposit, substantially more scale is dissolved at a faster rate than is possible without the synergist.

+ See back of page

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|------------------------------|----|---------------------------------------|----|--------------------------|
| AT | Austria | ES | Spain | MG | Madagascar |
| AU | Australia | FI | Finland | ML | Mali |
| BB | Barbados | FR | France | MR | Mauritania |
| BE | Belgium | GA | Gabon | MW | Malawi |
| BF | Burkina Faso | GB | United Kingdom | NL | Netherlands |
| BG | Bulgaria | HU | Hungary | NO | Norway |
| BJ | Benin | IT | Italy | RO | Romania |
| BR | Brazil | JP | Japan | SD | Sudan |
| CA | Canada | KP | Democratic People's Republic of Korea | SE | Sweden |
| CF | Central African Republic | KR | Republic of Korea | SN | Senegal |
| CG | Congo | LJ | Liechtenstein | SU | Soviet Union |
| CH | Switzerland | LK | Sri Lanka | TD | Chad |
| CM | Cameroon | LU | Luxembourg | TG | Togo |
| DE | Germany, Federal Republic of | MC | Monaco | US | United States of America |
| DK | Denmark | | | | |

SULFATE SCALE DISSOLUTION

This invention relates to sulfate scale dissolution. More particularly the invention relates to compositions and methods for dissolving an alkaline earth metal sulphate scale, especially strontium and barium sulphate scale. The invention is particularly useful for the removal of such scale from oilfield equipment including downhole pipe, tubing and casing as well as subterranean formations. It is also applicable to the removal of these scale deposits from other equipment such as boilers and heat exchangers.

Reference is hereby made to our copending patent application of even date entitled "Method of Decontaminating Earth and/or Natural Gas Processing Equipment". Many waters contain alkaline earth metal cations, such as barium, strontium, calcium and magnesium, and anions, such as sulfate, bicarbonate, carbonate, phosphate, and fluoride. When combinations of these anions and cations are present in concentrations which exceed the solubility product of the various species which may be formed, precipitates form until the respective solubility products are no longer exceeded. For example, when the concentrations of the barium and sulfate ions exceed the solubility product of barium sulfate, a solid phase of barium sulfate will form as a precipitate. Solubility products are exceeded for various reasons, such as evaporation of the water phase, change in pH, pressure or temperature and the introduction of additional ions which can form insoluble compounds with the ions already present in the solution.

As these reaction products precipitate on the surfaces of the water-carrying or water-containing system, they form adherent deposits or scale. Scale may prevent effective heat transfer, interfere with fluid flow, facilitate corrosive processes, or harbor bacteria. Scale is an expensive problem in many

industrial water systems, in production systems for oil and gas, in pulp and paper mill systems, and in other systems, causing delays and shutdowns for cleaning and removal.

Barium and strontium sulfate scale deposits present a unique and particularly intractable problem. Under most conditions, these sulfates are considerably less soluble in all solvents than any of the other commonly encountered scale-forming compounds, as shown by the comparative solubilities given in Table 1 below.

Table 1
Comparative Solubilities, 25°C in Water.

| <u>Scale</u> | <u>Solubility, mg./l.</u> |
|-------------------|---------------------------|
| Gypsum | 2080.0 |
| Strontium sulfate | 140.0 |
| Calcium Carbonate | 14.0 |
| Barium sulfate | 2.3 |

It is generally acknowledged that barium sulfate scale is extremely difficult to remove chemically, especially within reasonably short periods of time: the solvents which have been found to work generally take a long time to reach an equilibrium concentration of dissolved barium sulfate, which itself is usually of a relatively low order. Consequently, barium sulfate must be removed mechanically or the equipment, e.g. pipes, etc., containing the deposit must be discarded.

The incidence of barium sulfate scale is worldwide, and it occurs principally in systems handling subsurface waters. Because of this, the barium sulfate scale problem is of particular concern to the petroleum industry as water is generally produced with petroleum and as time goes on, more petroleum is produced by the waterflooding method of secondary

recovery, implying even greater volumes of produced water. The scale may occur in many different places, including production tubing, well bore perforations, the area near the well bore, gathering lines, meters, valves and in other production equipment. Barium sulfate scale may also form within subterranean formations such as in disposal wells. Scales and deposits can be formed to such an extent that the permeability of the formation is impaired resulting in lower flow rates, higher pump pressures, and ultimately abandonment of the well.

Barium sulfate scale is particularly troublesome when sulphate-rich seawater is used as an injection fluid in oil wells whose formation water is rich in barium ions. This particular aspect of the barium scale problem is severe in some U.S. oil fields as well as some older North Sea oil fields. Scaling of this nature is also expected to occur during advanced production stages in other North Sea fields particularly after seawater breakthrough has taken place.

Another problem associated with the formation of barium and strontium sulfate scales is that radium, another member of the alkaline earth group of metals tends to be deposited at the same time so that the equipment becomes radioactive, and may eventually have to become unusable for safety reasons alone. At present, a considerable amount of oilfield tubular goods are in this condition and cannot be readily restored to usable condition because of the difficulty of removing the radioactive scale.

Various proposals have been made in the past for removing barium sulfate scale chemically. Most of these processes have utilised chelating or complexing agents, principally the polyaminopolycarboxylic acids such as ethylenediaminetetraacetic acid(EDTA) or diethylenetriaminepentaacetic acid(DTPA).

US-A-2877848 discloses the use of EDTA in combination with various surfactants for this purpose. US-A-3660287 discloses the use of EDTA and DTPA in the presence of carbonate ion at

relatively neutral pH (6.5-9.5) and US-A-4,708,805 discloses a process for the removal of barium sulfate scale by sequestration using an aqueous solution of citric acid, a polycarboxylic acid such as carbazic acid, and an alkylene-polyaminopolycarboxylic acid such as EDTA or DTPA. The preferred aqueous sequestering solutions have a pH in the range of about 9.5 to about 14, provided by a base such as potassium hydroxide or potassium carbonate.

Another approach which has recently been made is to use a polyether in combination with the aminopolycarboxylic acid. US-A-4,190,462 discloses that barium sulfate scale can be removed from remote locations extending into a subterranean earth formation by contacting the scale with an aqueous solution consisting essentially of water, a monovalent cation salt of a monocyclic macrocyclic polyether containing at least two nitrogen-linked carboxymethyl groups and enough monovalent basic compound to provide a solution pH of about 8. Similar disclosures are to be found in US-A-4,215,000 and US-A-4,288,333. These polyether materials have, however, the disadvantage of being costly which is a severe drawback for oilfield use where cost is a major factor.

Although many of these known compositions will remove scale, the rate of dissolution is slow and the amount of scale dissolved is small.

We have now found a way of removing barium sulfate scale using various novel combinations of scale-removing agents. These combinations are capable of removing scale at markedly higher speeds than prior scale-removing compositions and are also capable of removing relatively more scale for a given quantity of solvent. They are, moreover, relatively cheap and are therefore well suited to use in oilfield operations.

Broadly, the invention relates to a composition and method for dissolving an alkaline earth metal sulfate scale. In a broad aspect the composition comprises:

- (a) an aqueous solution having a pH of from substantially 8 to substantially 14;
- (b) a chelating agent comprising an aminocarboxylic acid, polyaminocarboxylic acid, polyamine, salts thereof, or mixtures thereof; and
- (c) a scale-dissolving quantity of a synergist or catalyst.

Furthermore, in a broad aspect the method comprises contacting the scale with an aqueous solution having a pH of substantially 8 to substantially 14, which solution comprises: a chelating agent comprising an aminocarboxylic acid, a polyaminocarboxylic acid, a polyamine, a salt thereof, or mixtures thereof, and a scale-dissolving quantity of a synergist.

The aqueous solution is contacted with the scale for a time and at a temperature sufficient to dissolve it.

In one aspect of the invention the catalyst is selected from a member of the group consisting of anions of organic or inorganic acids and mixtures thereof, having an ionization constant greater than substantially a pK_a of 1. The ionization constant advantageously has an ionization constant (K_a) of less than substantially 10^{-2} ($K_a < 10^{-2}$). This enables a composition to be provided which can dissolve substantially more of the scale within a substantially reduced time period than is possible with the chelating agent alone. In this aspect of the invention, the catalyst may include fluoride anions, oxalate anions, persulfate anions, dithionate anions, hypochlorite anions, formate anions, thio anions, amino anions, hydroxyacetate anions. The preferred

anions in the catalyst are oxalate, thiosulphate, nitriloacetate and monocarboxylic acid anions.

In another aspect of the invention the synergist or catalyst comprises oxalate anions, thiosulphate anions, nitriloacetate anions or monocarboxylic acid anions.

In this aspect of the invention the chelating agent is advantageously a polyaminocarboxylic acid or a salt of such an acid.

In both aspects of the invention scale the constituents are preferably selected such that about 80% to about 90% of a solution level of barium, strontium or calcium sulfate is dissolved from powdered scale in about 10 minutes at a temperature of about 100°C.

In another aspect the invention provides a method for selecting a catalyst suitable for enhancing the dissolution of an alkaline earth metal sulphate when used in combination with a chelating agent selected from a member of the group consisting of an aminocarboxylic acid, a polyaminocarboxylic acid, a polyamine, salts thereof or mixtures thereof, comprising:

selecting said catalyst from anions having a negative free energy of reaction for the conversion of barium sulfate to barium compound which catalyst provides for substantially increased rates of dissolution of said scale than is possible with said agent alone.

The invention can also be applied to the reduction of the radioactivity of oilfield tubular goods contaminated with radium-containing scale of deposited alkaline metal sulfates. This method involves contacting the scale or the aqueous solution with one of the aqueous compositions described above for a time sufficient to remove the scale from the tubular goods.

In both the above aspects of the invention the concentration of synergist or catalyst is usually about 0.01 M to about 1.0 M, preferably about 0.5 M, with similar concentrations

being appropriate for the primary chelant (the polyaminopolycarboxylic acid). Substantially improved scale dissolution rates are obtained when the aqueous solution containing the composition is at a temperature of about 25°C to about 100°C, but higher temperatures are obtainable downhole because at greater formation depths higher existing pressures will raise the boiling point of the aqueous solution, and consequently greater scale removal rates may be attained.

In accordance with the present invention, alkaline earth metal sulfate scales, especially barium sulfate scale, are removed by the use of a combination of chemical scale-removing agents. The method is particularly useful for the removal of such scale from oilfield equipment used to bring oil and/or water from subterranean formations to the surface. The method may, however, also be used to remove scale from the formations themselves, especially in the regions surrounding production and injection wells, as mentioned above. The method may also be used to remove scale from above-ground equipment both in the oilfield and elsewhere, for example, from boilers and heat exchangers and other equipment exposed to scale-forming conditions.

The scale itself is usually in the form of an adherent deposit of the scale-forming mineral on metal surfaces which have been exposed to the water containing the scale-forming components. These components comprise alkaline earth metals including calcium, strontium and barium, together with variable amounts of radium, depending upon the origin of the waters. As noted above, barium sulfate scale is particularly difficult to remove by existing chemical methods in view of its very low solubility.

The present scale removal is effected with an aqueous solvent which comprises a polyaminopolycarboxylic acid such as EDTA or DTPA as a chelant or chelating agent which is intended to form a stable complex with the cation of the alkaline earth

scale-forming material. Of these chelants, DTPA is the preferred species since it forms the most soluble complexes at greatest reaction rate. EDTA may be used but is somewhat less favorable and, as noted below, may be less responsive to the addition of the catalyst or synergist. The chelant may be added to the solvent in the acid form or, alternatively, as a salt of the acid, preferably the potassium salt. In any event the alkaline conditions used in the scale removal process will convert the free acid to the salt.

The concentration of the chelant in the solvent should normally be at least 0.1M in order to achieve acceptable degree of scale removal. Chelant concentrations in excess of 1.0 M are usually not necessary and concentrations from about 0.3M up to about 0.6M will normally give good results; although higher concentrations of chelant may be used, there is generally no advantage to doing so because the efficiency of the chelant utilisation will be lower at excess chelant concentrations. This economic penalty is particularly notable in oilfield operations where large volumes of solvent may be used, especially in formation scale removal treatment.

As noted above, the catalyst is preferably an oxalate, thiosulfate, nitriloacetate or monocarboxylic acid anion.

The oxalate may be added as the free acid or the salt, preferably the potassium salt. If the free acid is used, addition of the potassium base to provide the requisite solution pH will convert the acid to the salt form under the conditions of use.

Thiosulfate salts, especially sodium thiosulfate or potassium thiosulfate provide a suitable source of the thiosulfate anion since the acid itself is unstable; these salts are, moreover, readily available commercially at reasonable cost.

Nitriloacetate anions may be supplied by the acid itself, which is converted to the salts under the pH conditions employed,

or by the addition of a nitriloacetate salt. Nitriloacetic acid, otherwise known as triglycine, $N(CH_2COOH)_3$, is an acid which is insoluble in water but which readily forms water soluble mono-, di-, and tribasic salts from various cations including the alkali metals, especially sodium and potassium. The addition of the free acid to the solvent will therefore result in dissolution under the pH conditions prevailing. Alternatively, the nitriloacetate anions may be added by addition of the nitriloacetate salts, especially the sodium or potassium salts. In either case, the alkaline conditions will result in the formation of the tribasic nitriloacetate anion, $N(CH_2COO)_3^{3-}$, in the solvent. The potassium salts are preferred in view of their greater solubility and for this reason, the solvent should preferably be brought to the desired pH value with a potassium base, preferably potassium hydroxide.

When the catalyst is an anion or anions of at least one monocarboxylic acid, the acid may be substituted with various functional groups, especially electronegative groups such as hydroxyl, amino, halo or mercapto or may be unsubstituted. The lower substituted fatty acids such as the C_1 - C_3 substituted fatty acids where the substituent is an electronegative group such as hydroxy, mercapto, or amino are suitable since they have good solubility in oilfield waters, are readily available and are relatively inexpensive. Suitable acids of this type include mercaptoacetic acid, aminoacetic acid and hydroxyacetic acid. The unsubstituted fatty acids such as acetic acid and formic acid have not been found to provide any major improvement in scale removal with DTPA as a chelant and are therefore not preferred. The aromatic carboxylic acids may also be used when they have an adequately high solubility in water. The acid may have substituents other than the carboxyl group on the aromatic nucleus, for example, hydroxyl as in salicylic acid which is a preferred acid of this type. Other aromatic carboxylic acids

with carboxyl groups attached directly to the aromatic nucleus may also be used. The preferred acids have been found to enhance the rate of barium sulfate scale dissolution using polyaminopolycarboxylic chelants, especially DTPA, to a significant and useful degree, so that dissolution of oilfield scales is usefully accelerated by the use of these compositions.

It has been found that the action of the synergist may be selective for the chelant. For example, salicylate produces a significant increase in scale removal with the chelant DTPA but only a slight improvement with EDTA. The use of DTPA is therefore favored not only because it generally shows an improved propensity in itself to remove the alkaline earth metal sulfate scales but also because it exhibits better response to a number of these synergists.

The carboxylate synergist may be added as the free acid or the salt, preferably the potassium salt. If the free acid is used, the addition of the potassium base to provide the requisite solution pH will convert the acid to the salt form under the conditions of use.

The concentration of the catalyst or synergist in the aqueous solvent will be of a similar order to that of the chelant: thus, the amount of the synergist anion in the solvent should normally be at least 0.1M in order to achieve a perceptible increase in the efficiency of the scale removal, and concentrations from about 0.3M up to about 0.6M will give good results. Although higher concentrations of the synergist e.g. above 1.0 M may be used, there is generally no advantage to doing so because the efficiency of the process will be lower at excess catalyst concentrations. Again, this economic penalty is particularly notable in oilfield operations.

The scale removal is effected under alkaline conditions preferably at pH values of from about 8.0 to about 14.0, with optimum values being from about 11 to 13, preferably about 12.

The preferred solvents comprise about 0.1 to about 1.0 M of ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA), or salts of these acids, as a chelant. In addition, the oxalate, thiosulfate, nitriloacetate or carboxylic anion as the catalyst or synergist is added to the aqueous solution in about 0.01 to about 1.0, preferably about up to 0.5 M. The pH of the solvent is then adjusted by the addition of a base, to the desired value, preferably to about pH 12. The base may be a hydroxide of lithium, sodium, potassium or cesium, but potassium is preferred. We have found that it is important to avoid the use of sodium cations when operating at high pH values, above pH 8, and instead, to use potassium or, alternatively, cesium as the cation of the scale-removing agent. Potassium is preferred for economy as well as availability. Thus, the normal course of making up the solvent will be to dissolve the chelant and the acid synergist (or its potassium salt) in the water to the desired concentration, after which a potassium base, usually potassium hydroxide is added to bring the pH to the desired value of about 12. This aqueous composition can be used to remove scale from the equipment, or alternatively, pumped into the subterranean formation when it is the formation which is to be subjected to descaling.

The mode of operation of the synergist or catalyst is not presently understood. While not desiring to be bound to a particular theory concerning the actual mechanism of its activity in converting or dissolving the scale, it is believed that adsorption of the synergist or catalyst on the barium sulfate surface may modify the surface crystal structure in such a way that the barium in the modified crystal is easily removed by the chelating agent.

The aqueous solution containing the composition can be directed down a wellbore to remove barium sulfate scale which has

fouled the tubular equipment e.g. piping, casing etc., and passage ways. Prior to being directed into the wellbore, the composition may be heated to a temperature between about 25°C to about 100°C., although the temperatures prevailing downhole may make pre-heating unnecessary. Once within the tubular goods and the passageways requiring treatment, the composition is allowed to remain there for about ten minutes to about 7 hours. After remaining in contact with the equipment for the desired time, the composition containing the dissolved scale is produced to the surface and may be disposed of as required, possibly by re-injection into the subsurface formation. This procedure can be repeated as often as required to remove scale from the equipment.

In one procedure for circulating the solvent through the tubular goods in the well the solvent is pumped down through the production tube and returned to the surface through the annular space between the production tubes and the casing (or vice versa). Also, the cleaning solution may be pumped down through the production tubing and into the formation, thereby cleaning the well, including the well casing, and the formation pore space by dissolving barium sulfate present as it flows over and along the surfaces that need cleaning. The spent composition containing the dissolved, complexed barium together with any other alkaline earth metal cations which may have been present in the scale, especially radium, can be subsequently returned to the surface, for example, by displacement or entrainment with the fluids that are produced through the well after the cleaning operation. In an alternative manner, the cleaning solution may be applied batchwise fashion, for example, by flowing the solution into the well and optionally into the pore spaces of the adjacent earth formation and there keeping the solution in contact in non-flowing condition with the surfaces that are

covered with barium sulfate scale, for a period of time sufficient to dissolve the scale.

The present scale removal technique is very effective for lowering residual radioactivity of pipe contaminated with radium-containing barium sulfate scale. As noted above, radium is frequently precipitated with barium in scale with the result that scaled pipe is often radioactive to the point that it cannot safely be used. Using the present scale removal compositions, activity can be reduced to an acceptable level in comparatively short times without further treatment. Some residual activity arises from lead and other radio-isotopes which are not dissolved in the solvent: these isotopes are decay products of radium and have originally been incorporated in the scale with the barium and the radium sulfates. Although they are not removed chemically by the present scale removal technique, the dissolution of the barium scale together with the other alkaline earth metal sulfates enables these other components of the scale to be removed by simple abrasion, for example, by scrubbing with or without a detergent/water scrub solution. In this way, the residual activity level may be reduced to a very low value, below the appropriate regulatory standards. Thus, by using the present chemical scale removal technique in combination with a simple mechanical removal of loose, non-adherent material, previously radioactive pipe may quickly and readily be restored to useful, safe condition.

Reference is now made to the accompanying drawings in which:

Figure 1 is a graph which depicts the dissolution efficiency of barium sulfate as a function of ligand concentration;

Figure 2 is a graph which depicts the free energy of reaction for barium sulfate conversion at 25°C;

Figure 3 is a graphical representation of the rate of barium sulfate dissolution in the presence of a solution having a pH of 12, 0.5 M DTPA, and varying concentrations of an oxalate catalyst at a temperature of 100°C.

Figure 4 is a graph which shows the effect of chelant concentration on the rate of barium sulfate dissolution;

Figure 5 is a graphical representation of the rate of barium sulfate dissolution in 0.5 M EDTA with catalysts of 0.5 M oxalate, 0.5 M potassium fluoride and 0.5 M potassium acid tartrate;

Figure 6 is a graph depicting the rate of barium sulfate dissolution in 0.5 M DTPA with catalysts of 0.5 M potassium fluoride, 0.5 M oxalate, and 0.5 M potassium acid tartrate at 25°C.

Figure 7 is a graph which shows the rate of dissolution of barium sulphate in various solvents;

Figure 8 is a graph which depicts the rate of barium sulfate dissolution in 0.5 M DTPA with catalysts of 0.5 M potassium fluoride and 0.5 M oxalate at various temperatures;

Figure 9 is a graph which shows effect of temperature on the rate of barium sulfate dissolution,

Figure 10 is a graph which shows the respective rates of dissolution of various sulfate species on a chelant-containing solvent,

Figure 11 is a graph which shows the respective rates of dissolution of various barium sulfate species in a chelant-containing solvent,

Figure 12 is a graph which shows the low residual rates of radioactivity which may be achieved for contaminated oilfield pipe by use of the present scale removal process.

Figure 13 is a graph which shows the rate of dissolution of barium sulfate in solutions of DTPA containing various substituted acetic acids as synergists.

Figure 14 is a graph which shows the rate of dissolution of barium sulfate in solutions of DTPA containing salicylic acid as a synergist; and

Figure 15 is a graph which shows the rate of dissolution of barium sulphate in solutions of DTPA containing thiosulphate or nitrilotriacetate anion as a synergist.

The compositions and methods according to the invention are particularly useful for more efficiently removing barium or strontium sulfate scale from wells, wellstream processing equipment, pipelines and tubular goods used to produce oil from a subterranean formation.

In order to demonstrate the barium sulfate scale-dissolving capacities of the composition, several aqueous solutions have been tested in laboratory tests the results of which are described in the discussions which follow. The experiments described below were, except as noted below, carried out in a cylindrical glass vessel having a height of 10 cm and an internal diameter of 7.5 cm. Barium sulfate, or where applicable, other solid scale components were added to the test solution and agitated with the selected solvents and the rates of dissolution and final dissolved concentrations determined. The results are reported graphically in the figures.

As shown in Figure 1, varying concentrations of DTPA and EDTA are compared with 2.2.2-cryptand which is described in US-A-4,215,000. As described, various concentrations of DTPA with oxalate and EDTA were compared with the barium sulfate dissolution of 2.2.2-cryptand. The results were obtained at 25°C and demonstrate that DTPA/oxalate complexes more barium sulfate (49 g/l) than 2.2.2-cryptand (37 g/l). As the dotted lines in the graph reveal, DTPA/oxalate is substantially more efficient than either 2.2.2-cryptand or an EDTA chelant at all concentrations. Efficiency of a chelant or solvent is defined as

the fraction of chelant that is complexed with barium divided by the total concentration of chelating agent.

The amount of oxalate catalyst utilized in combination with DTPA is not critical, within the limits described above. This is illustrated in Figure 3 which shows that all concentrations of oxalate catalyst from 0.1 to 0.5M contribute to the dissolution of 80 to 90 percent of the saturation level of barium sulfate within ten (10) minutes of contact. Additionally, as demonstrated in Figure 3, the fast rate of dissolution is a significant feature of the present scale removal technique. In practical applications of the methods therefore, contact times of less than about 4 hours, eg. 1 or 2 hours, may be sufficient, depending on the scale thickness. Another significant feature of the technique is the high equilibrium (saturation) levels of dissolved barium, strontium and calcium sulfate scales which are obtained in the aqueous solution, making the process particularly efficient in terms of solvent utilisation.

Barium sulfate or other scales dissolved in the solvent are influenced by the concentration of chelant used. The effect of varying the DTPA concentration (100°C) is depicted in Figure 4 at chelant concentrations from 0.1M to 0.6M. Increased DTPA concentration causes an increase in the rate of barium sulfate dissolution and the amount of barium sulfate held in the solvent. It should be noted in particular that the final equilibrium concentration of barium sulfate is 60 g/l which is far in excess of the solubility in water alone.

Figure 5 illustrates the rate of barium sulfate dissolution when 0.5 M EDTA is used with 0.5 M catalysts including oxalate, potassium fluoride and potassium hydrogen tartrate. Figure 5 also illustrates the barium sulfate dissolution rate when 0.5 M EDTA is used alone. The temperature of the solvent in which the catalyst is used affects the rate of barium sulfate or scale dissolution. This is further shown in

Figure 6. Here differences in the barium sulfate or scale dissolution rate of a solvent containing 0.5 M DTPA is shown when the temperature is maintained at 100°C and 25°C with designated catalysts. These catalysts comprise 0.5 M potassium fluoride, 0.5 M oxalate and 0.5 M potassium acid tartrate.

Effectiveness of an oxalate catalyst is shown with DTPA when compared to DTPA alone at 25°C and 100°C. This is illustrated in Figure 7. DTPA with oxalate at 25°C has nearly the same barium sulfate dissolution rate as DTPA only at a temperature of 100°C. Examining Figure 7, it is readily apparent that the oxalate catalyst caused the difference. This is apparent since the barium sulfate dissolution rate of DTPA with oxalate at 25°C is much greater than the dissolution rate of barium sulfate by DTPA alone at 25°C. As illustrated in Figure 7, about 90 percent of the scale is dissolved in the lab within the first ten minutes of contact, using Powdered BaSO₄. Much slower rates of barium sulfate dissolution are shown when EDTA and DTPA are utilized without a catalyst at 25°C. The results show that the DTPA/oxalate combination complexes more barium sulfate than DTPA alone and that DTPA is more effective than EDTA at both temperatures. Furthermore when the oxalate is present with the DTPA, the equilibrium concentration of dissolved barium sulphate is reached far more quickly than with either the EDTA or the DTPA, which have not achieved equilibrium after 7 hours at the termination of the experiment.

Although catalysts greatly enhance the rate of barium sulfate dissolution by DTPA or EDTA, this enhancement varies with the particular catalyst employed. Figure 8 illustrates graphically the difference in barium sulfate dissolution when selected catalysts are utilized with DTPA. These catalysts comprise 0.5 M potassium fluoride at 100°C and 25°C, and 0.5 M oxalate at 25°C.

As mentioned above, the rate of barium sulfate scale dissolution varies with the solvent composition utilized. In order to determine candidates for use as a solvent, free energy calculations for the conversion of barium sulfate to barium carbonate were utilized. This is a well known conversion using concentrated sodium carbonate solution and solid alkaline earth metal sulfates. Free energy of conversion of barium sulfate to barium carbonate is calculated as essentially zero, meaning that the conversion is energetically favorable. However, the conversion is expected to reach equilibrium with less than full conversion of barium sulfate to barium carbonate. This is the actual reaction situation with only about 75-80 percent of the barium sulfate being converted. Further calculations were made using common anions, both organic and inorganic. Some of the anions considered are shown in Figure 2 of the free energy graph. Those anions with a negative free energy of reaction are considered very reactive toward conversion of alkaline earth sulfates to the respective barium compounds. Many of the anions are by nature strong oxidizing agents, for example, persulfate (S_2O_8), dithionate (S_2O_6), and hypochlorite (OCl), normally would not be considered practical for use in a hydrocarbon environment. Fluoride (F^-) and oxalate ($C_2O_4^{2-}$) anions are found to be very active catalysts for ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) or their salts for dissolution of barium sulfate, respectively. Experimentally, it was determined that the catalysts alone (without EDTA OR DTPA) have no scale dissolution properties of their own.

Oxalic acid or salts are used to obtain oxalate anions. Salicylic acid, the precursor to aspirin, is also an effective catalyst for dissolution of barium, strontium and calcium sulfates in combination with DTPA. Experiments indicate that it has a higher rate of dissolution and saturation level than oxalate anions. Both oxalic and salicylic acids are commercially

available and are relatively inexpensive. For 0.1 to 0.5 molar concentrations, salicylic acid would add US\$5 to US\$24 per barrel for chemical cost, whereas oxalic acid would contribute from about US\$2 to US\$7 to the cost per barrel.

Salicylic acid is used to obtain salicylic anions. Effective catalyst anions are also obtainable from aminoacetic acid (glycine), glycolic acid (hydroxyacetic acid), and thioglycolic acid (mercaptoacetic acid).

One example of a preferred aqueous solvent which can be used comprises 0.5M DTPA and 0.3M Oxalic acid adjusted to a pH of 12 with potassium hydroxide.

Another example of a preferred aqueous solvent for use herein comprises 0.5M EDTA and 0.5M KF adjusted to a pH of 12 with potassium hydroxide.

Figure 9 shows that the rate of dissolution of the barium sulfate scale is related to temperature, with faster rates of dissolution being attained at the higher temperature ($0^{\circ}\text{C}.$)

Figure 10 shows the results of a batch test carried with scale material removed from field tubing similar to that used in a continuous flow loop test in which the test solution was circulated. The samples of scale material were added to the solvent (0.5M DTPA, 0.5M oxalate pH=12, $0^{\circ}\text{C}.$) in a concentration equivalent to 60 g./l. of scale. The concentrations of the different species dissolved in the solvent at different times were determined. The results of the batch tests are shown in figure 10 and indicate that in addition to the dissolution of the barium, the strontium sulfate also reaches equilibrium concentration in a very short time. The results from the flow loop tests are similar but with much lower final concentrations.

Figure 11 shows that the scale removal process is effective both with barium sulfate in the powder form and also with actual pipe scale/tar mixtures and with barite ore (BaSO_4).

Figure 12 shows that the present scale removal technique is very effective for lowering residual radioactivity of pipe contaminated with radium-containing barium sulfate scale. As noted above, radium is frequently precipitated with barium in scale with the result that scaled pipe is often radioactive to the point that it cannot safely be used. A continuous flow loop test was used to remove the scale from pipe which was similar to that used with Figure 5 and the radioactivity was determined at successive times during the test. As shown in the Figure, the activity was reduced to an acceptable level after three hours without further treatment. It appears, however, that some residual activity arises from lead and other radio-isotopes which are not dissolved in the solvent (see Fig.5); these isotopes are decay products of radium and have originally been incorporated in the scale with the barium and the radium sulfates. Although they are not removed chemically by the present scale removal technique, the dissolution of the barium scale together with the other alkaline earth metal sulfates enabled these other components of the scale to be removed by simple abrasion. For Figure 7, the descaled pipe was scrubbed with a soft bristle brush using a detergent/water scrub solution. The result was to reduce the residual activity level to a very low value, below the appropriate regulatory standards. Thus, by using the present chemical scale removal technique in combination with a simple mechanical removal of loose, non-adherent material, previously radioactive pipe may quickly and readily be restored to useful, safe condition.

As shown in Figure 13, DTPA alone and DTPA with various substituted acetic acids were compared at 100°C. The results demonstrate that the DTPA/carboxylate combination complexes more barium sulfate than DTPA alone.

Figure 14 compares the relative rates of barium sulfate dissolution using DTPA alone and DTPA in combination with

salicylic acid. As shown in the Figure, the addition of salicylic acid is effective to almost double the degree of barium sulfate dissolution.

Referring to figure 15, the solvents used comprised 0.5M DTPA in combination with either 0.5M thiosulfate added as potassium thiosulfate, $K_2S_2O_3$, or 0.1M nitriloacetate, added as nitriloacetic acid, with the required pH of 12 attained by the addition of potassium hydroxide. The results are reported graphically in the Figure.

As shown in Figure 15, DTPA alone and DTPA with thiosulfate and nitriloacetate synergists were compared at 100°C. The results demonstrate that the DTPA/synergist combination complexes more barium sulfate than DTPA alone, and that thiosulfate is slightly more effective as a synergist than nitriloacetate. Although the nitriloacetate catalyst was initially less effective than the chelant alone, the final equilibrium concentration of the dissolved scale component became greater at contact times longer than about 100 minutes, so that there is a potential for scale removal with this synergist at extended contact times using this low proportion of the synergist.

Distilled water was used in the tests shown in Figure 15, and with the majority of the other tests (except the continuous flow loop tests). Minor decreases in efficiency may be observed with tap water and more significant decreases with seawater, e.g. about 20 percent decrease with seawater. This is reasonably to be expected since seawater has interfering ions, e.g. calcium and magnesium. These interfering ions complex with the chelating agent, either DTPA or EDTA, and reduce the overall dissolving power. Additionally, it has been determined that halide ions have a negative effect on dissolving power as a function of the size of the halide ion. Dissolution rate is increased as the halide ion size is reduced and the charge density is increased,

i.e. in the order of iodide, bromide, chloride and fluoride. Fluoride ion enhances the effect of EDTA-based solvents, but not DTPA: fluoride inhibits most DTPA/catalyst solvents.

As noted above, the effect of cations is also very important to the success of the scale solvent, especially when added with the sizable portion of caustic required to adjust the pH to 12. Dissolution is enhanced as the size of the cation is increased, i.e. lithium, sodium, potassium and cesium. Lithium and sodium hydroxides in the presence of EDTA, or DTPA, and catalysts are not soluble at a pH of 12, the optimum value. Cesium is too difficult to obtain, both in quantity and price. Therefore, potassium hydroxide, in the form of caustic potash, is the pH adjusting reagent of choice.

Another effective chelant is cyclohexanediaminetetraacetic acid (CDTA), which may be used with any of the synergists disclosed hereinabove. CDTA is particularly useful with the oxalate anion at a pH of substantially 13.

CLAIMS

1. A composition for dissolving an alkaline earth metal sulfate scale comprising:
 - a) an aqueous solution having a pH of from substantially 8 to substantially 14;
 - b) a chelating agent selected from a member of the group consisting of aminocarboxylic acid, polyaminocarboxylic acid, polyamines, salts and mixtures thereof; and
 - c) a catalyst selected from a member of the group consisting of anions of organic or inorganic acids and mixtures thereof, having an ionization constant of less than substantially 10^{-2} ($K_a < 10^{-2}$).
2. A composition according to Claim 1 wherein the chelating agent is EDTA or DTPA and the catalyst comprises fluoride, oxalate, persulfate, dithionate, hypochlorite, formate, thio, amino, and/or hydroxy acetate anions.
3. A composition according to Claim 1 wherein the pH is adjusted to about 12 with potassium hydroxide, the chelant comprises EDTA and the catalyst comprises fluoride anions.
4. A composition according to Claim 1 wherein the pH is adjusted to about 12 with potassium hydroxide, the chelant comprises DTPA and the catalyst comprises oxalate anions.
5. A composition according to Claim 1 wherein the pH is adjusted to about 12 with potassium hydroxide, the chelant comprises DTPA and the catalyst comprises formate anions.

6. A composition according to Claim 1, wherein the catalyst comprises oxalate, thiosulfate, nitriloacetate or monocarboxylic acid anions:

7. A composition for dissolving an alkaline earth metal sulfate scale comprising:

(a) an aqueous solution having a pH of from substantially 8 to substantially 14;

(b) a chelating agent comprising a polyaminopolycarboxylic acid or a salt of such an acid; and

(c) a synergistic scale-dissolving quantity of oxalate, thiosulfate, nitriloacetate or monocarboxylic acid anions.

8. A composition according to Claim 1 or 7, wherein the pH is obtained by the addition of hydroxides of lithium, sodium, potassium or cesium.

9. A composition according to Claim 1 or 7 which is heated to a temperature of from substantially 25°C to substantially 100°C or higher depending upon the depth to which said composition is to be injected into a subterranean formation.

10. A composition according to Claim 1 or 7 wherein the chelating agent is DTPA.

11. A composition according to Claim 1 or 7 wherein the pH is obtained by the addition of hydroxides of potassium.

12. A composition according to Claim 1 or 7 wherein the chelating agent is present in an amount of 0.1M to 1.0M.

13. A composition according to Claim 12 wherein the chelating agent is in an amount of from 0.3M to 0.6M.

14. A composition according to Claim 1 or 7 wherein the synergistic anions are present in a concentration of from 0.1M to 0.6M.

15. A composition according to Claim 14 wherein the synergistic anions are present in a concentration of 0.3M to 0.6M.

16. A composition according to Claim 1 or 7 wherein the synergist comprises thiosulfate anions.

17. A composition according to Claim 1 or 7 wherein the synergist comprises nitriloacetate anions.

18. A composition according to Claim 1 or 7 wherein the synergist comprises monocarboxylic acid anions.

19. A composition according to Claim 1 or 7 wherein the synergist comprises oxalate anions.

20. A composition according to Claim 18 wherein the synergist comprises anions of a substituted acetic acid.

21. A composition according to Claim 20 wherein the substituted acetic acid is mercaptoacetic acid, hydroxyacetic acid or aminoacetic acid.

22. A composition according to Claim 1 or 7 wherein the synergist comprises anions of an aromatic carboxylic acid having the carboxyl group attached directly to the aromatic nucleus.

23. A composition according to Claim 22 wherein the synergist comprises anions of salicyclic acid.

23. A composition according to Claim 1 or 7 wherein the pH of the solution is from 10 to 13.

24. A composition according to Claim 23 wherein the pH of the solution is substantially 12.

25. An aqueous composition for dissolving alkaline earth sulfate scale comprising an aqueous alkaline solution having a pH of from substantially 8 to substantially 14, from substantially 0.05M to substantially 1.0M of a chelating agent comprising a polyaminopolycarboxylic acid or a salt of such an acid, and from substantially 0.05M to substantially 1.0M of a synergist comprising at least one anion selected from oxalate, thiosulfate, nitriloacetate and monocarboxylic acid to improve the scale removing characteristics of the composition.

26. A composition according to Claim 25 wherein the pH is obtained by the presence of a potassium base.

27. A composition according to Claim 25 wherein the chelating agent comprises DTPA.

28. A composition according to Claim 12 wherein the pH is adjusted to a value from substantially 11 to 13 with potassium hydroxide, the chelating agent comprises DTPA and the synergist anion is present in a concentration of from 0.3M to 0.6M.

29. A composition according to Claim 25 wherein the synergist comprises anions of a substituted acetic acid.

30. A composition according to Claim 29 wherein the substituted acetic acid is mercaptoacetic acid, hydroxyacetic acid or aminoacetic acid.

31. A composition according to Claim 25 wherein the synergist comprises anions of an aromatic carboxylic acid having the carboxyl group attached directly to the aromatic nucleus.

32. A composition according to Claim 31 wherein the synergist comprises anions of salicylic acid.

33. A method for removing alkaline earth scale comprising:

(a) contacting said scale with an aqueous solution having a pH of substantially 8 to substantially 14 which solution contains an aminocarboxylic acid, polyaminocarboxylic acid or polyamine chelant, salts or mixtures thereof, and a catalyst which comprises anions or organic or inorganic acids and mixtures thereof, where said acids have an ionization constant of less than substantially 10^{-2} ($K_a < 10^{-2}$) thereby making a solution which can dissolve substantially more scale within a substantially reduced time period than is possible with said chelant alone; and

(b) allowing said solution to remain in contact with said scale for a time sufficient and at a temperature sufficient to dissolve said scale.

35. A method according to Claim 34 wherein the chelating agent is EDTA or DTPA and the catalyst comprises fluoride, oxalate, persulfate, dithionate, hypochlorite, formate, thio, amino, and/or hydroxy acetate anions.

36. A method according to Claim 34, wherein the catalyst comprises oxalate, thiosulfate, nitriloacetate or monocarboxylic acid anions:

37. A method for removing alkaline earth sulfate scale comprising contacting the scale with an aqueous solution having a p^H of substantially 8 to substantially 14 and comprising a chelating agent comprising a polyaminopolycarboxylic acid or salt of such an acid, and a synergist anion selected from oxalate thiosulfate, nitriloacetate and monocarboxylic acid to dissolve the scale.

38. A method according to Claim 33 or 37 wherein the chelating agent comprises DTPA.

39. A method according to Claim 38 wherein the DTPA is present in a concentration of from 0.1M to 1.0M.

40. A method according to Claim 38 wherein the synergist anion is present in a concentration of from 0.1M to 1.0M.

41. A method according to Claim 33 or 37 wherein the pH of the solution is from 11 to 13.

42. A method according to Claim 41 wherein the pH of the solution is substantially 12.

43. A method according to Claim 33 or 37 wherein the scale is contacted with the solution at a temperature from 25°C to 100°C, or higher depending upon the depth to which the composition is injected into a subterranean location.

44. A method according to Claim 33 or 37 wherein the scale is contacted with the solution for a time up to 4 hours.
45. A method according to Claim 33 or 37 wherein the pH of the solution is provided by the use of a potassium base.
46. A method according to Claim 45 wherein the potassium base is potassium hydroxide.
47. A method according to Claim 33 or 37 wherein the scale comprises barium, strontium or calcium sulfate or mixtures thereof.
48. A method according to Claim 33 or 37 wherein substantially 80% to 90% of a saturation level of barium, strontium or calcium sulfate is dissolved from the scale in substantially 10 minutes at a temperature of substantially 100°C.
49. A method according to Claim 33 or 37 wherein the solution is directed down a cased wellbore, from which the scale is dissolved and subsequently dissolved scale is removed from the wellbore.
50. A method according to Claim 33 or 37 wherein the solution is contacted with a subsurface formation to remove scale from the formation.
51. A method according to Claim 33 or 37 wherein the sulfate scale contains radium.
52. A method according to Claim 37 wherein the synergist comprises anions of a substituted acetic acid.

53. A method according to Claim 52 wherein the substituted acetic acid is mercaptoacetic acid, hydroxyacetic acid or aminoacetic acid.

54. A method according to Claim 37 wherein the synergist comprises anions of an aromatic carboxylic acid having the carboxyl group attached directly to the aromatic nucleus.

55. A method according to Claim 54 wherein the synergist comprises anions of salicylic acid.

56. A method for reducing the radioactivity of oilfield tubular goods contaminated with radioactive, radium-containing scale or deposited alkaline earth metal sulfates, comprising contacting the scale on the tubular goods with an aqueous composition for dissolving alkaline earth sulfate scale comprising an aqueous alkaline solution having a pH of from substantially 8 to substantially 14, from substantially 0.05M to substantially 1.0M of a chelating agent comprising a polyaminopolycarboxylic acid or a salt of such an acid, and from substantially 0.05M to substantially 1.0M of a synergist anion selected from oxalate, thiosulfate, nitriloacetate and monocarboxylic acid anions to improve the scale removing characteristics of the composition, for a time sufficient to remove the scale from the tubular goods.

57. A method according to Claim 56, wherein the synergist is thiosulphate or nitriloacetate, and the pH is between substantially 11 and substantially 14.

58. A method according to Claim 56 wherein the chelating agent comprises DTPA in a concentration of from 0.1M to 1.0M, the synergist is in a concentration of from 0.1M to 1.0M, and the pH is from 11 to 13 provided by potassium hydroxide.

59. A method according to Claim 56 wherein the tubular goods are subjected to mechanical abrasion after removal of the scale by the solution.

60. A method according to Claim 56 wherein the scale is contacted with the solution at a temperature of from 25°C to 100°C.

61. A method for selecting a catalyst suitable for enhancing the dissolution of an alkaline earth metal sulfate scale when used in combination with a chelating agent selected from a member of the group consisting of aminocarboxylic acid, polyaminocarboxylic acid, polyamines, salts or mixtures thereof comprising:

selecting said catalyst from anions having a negative free energy of reaction for the conversion of barium sulfate to barium compound which catalyst provides for substantially increased rates of dissolution of said scale than is possible with said agent alone.

62. A method according to Claim 61 wherein said chelating agent is EDTA or DTPA, salts and mixtures thereof.

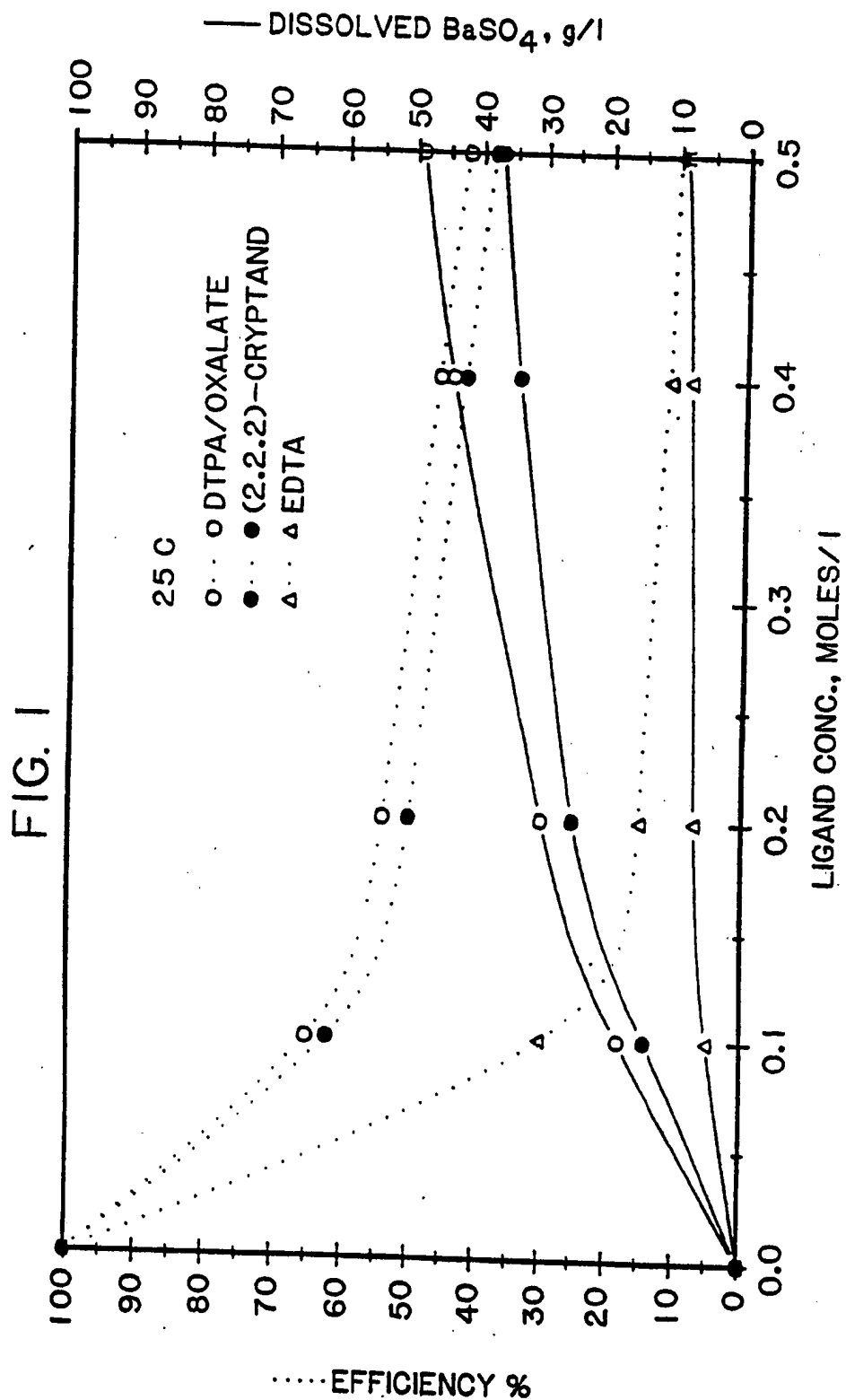
63. A method according to Claim 61 wherein said scale is barium sulfate.

64. S method according to Claim 61 wherein said catalyst comprises fluoride, oxalate, persulfate, dithionate, hypochlorite, and formate anions, also thio, amino, and/or hydroxy acetate anions.

32

65. A method according to Claim 61 wherein said catalyst comprises oxylate, thiosulphate, nitriloacetate or monocarboxylic acid anions.

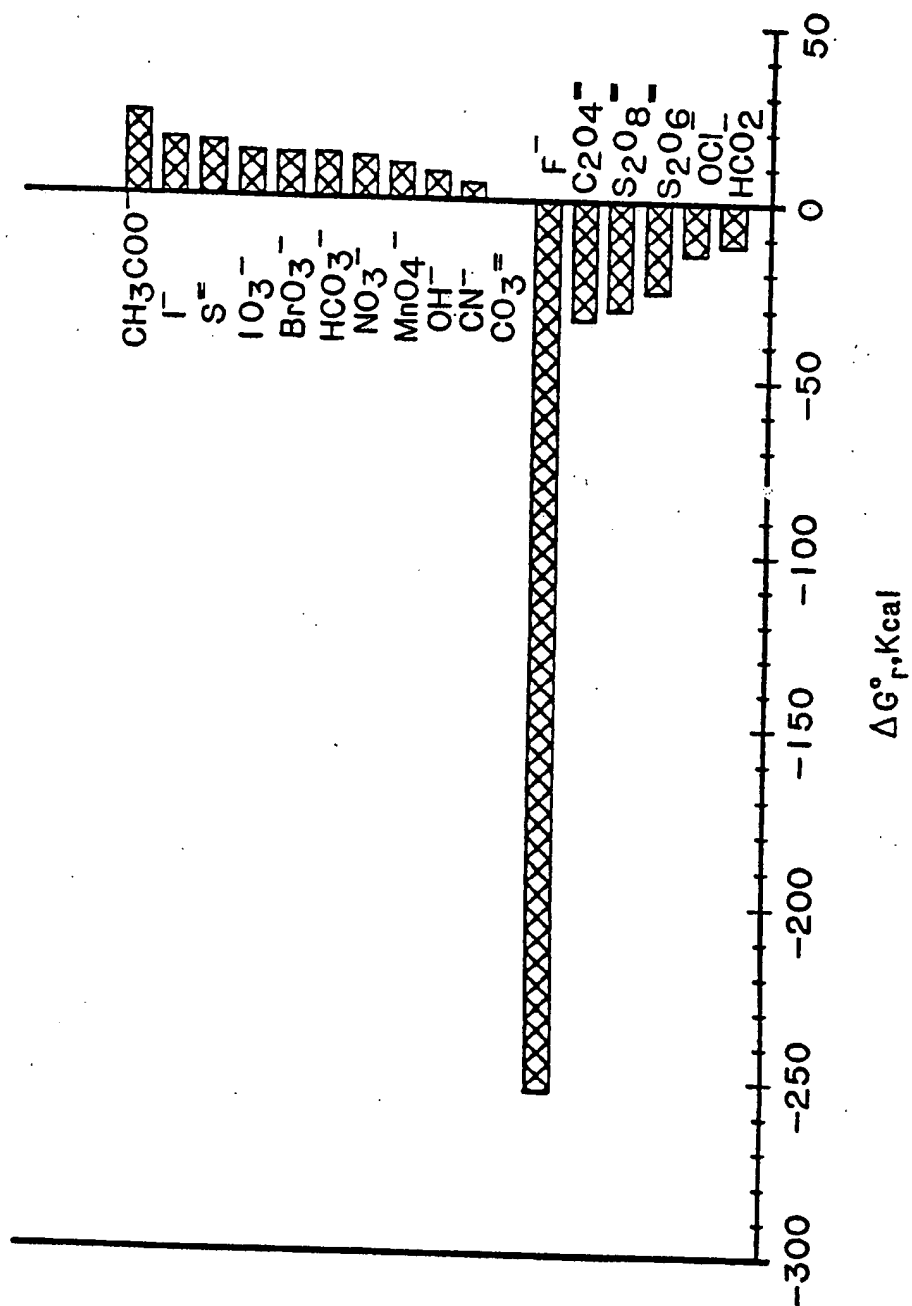
1 / 15



SUBSTITUTE SHEET

2 / 15

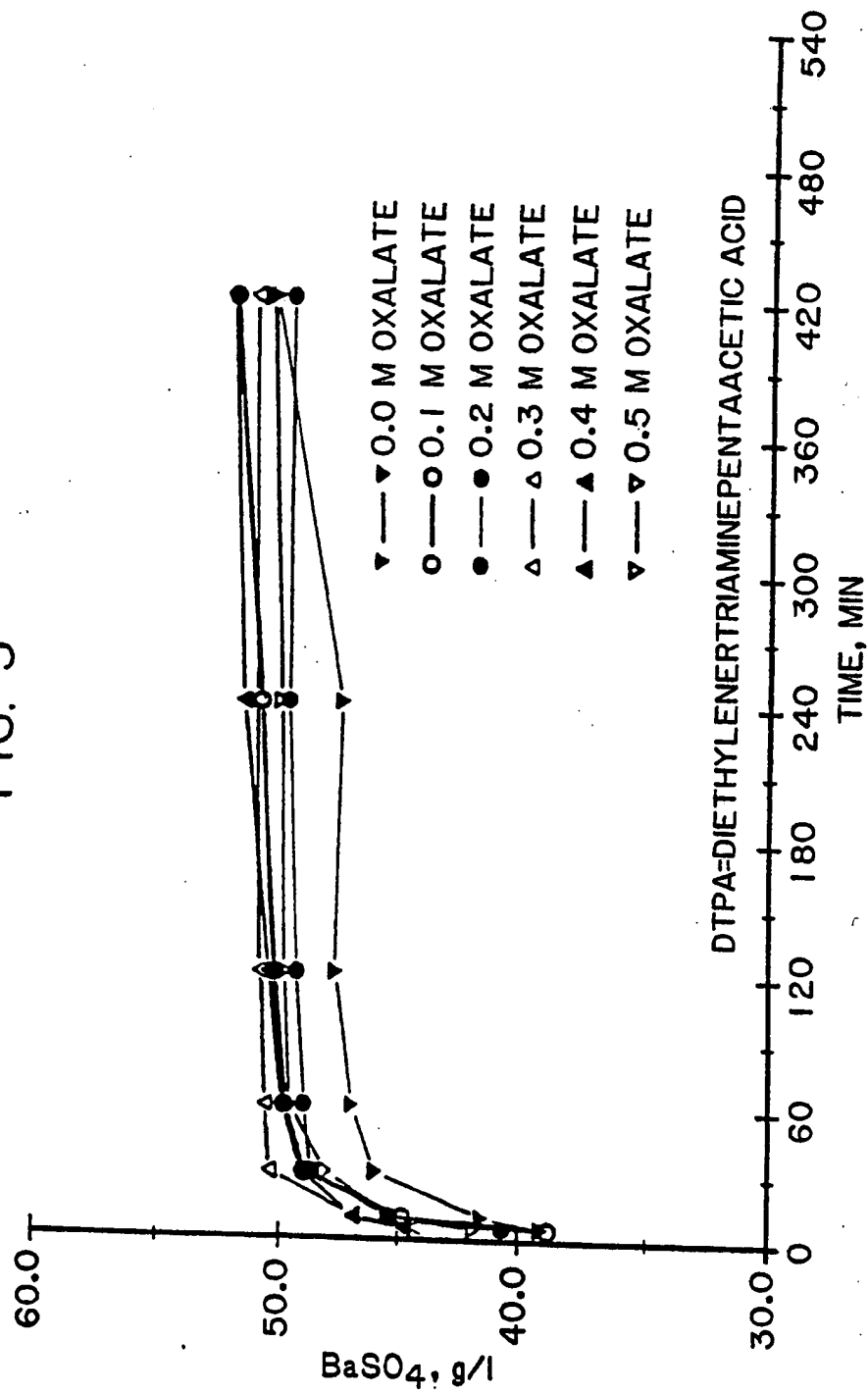
FIG. 2



SUBSTITUTE SHEET

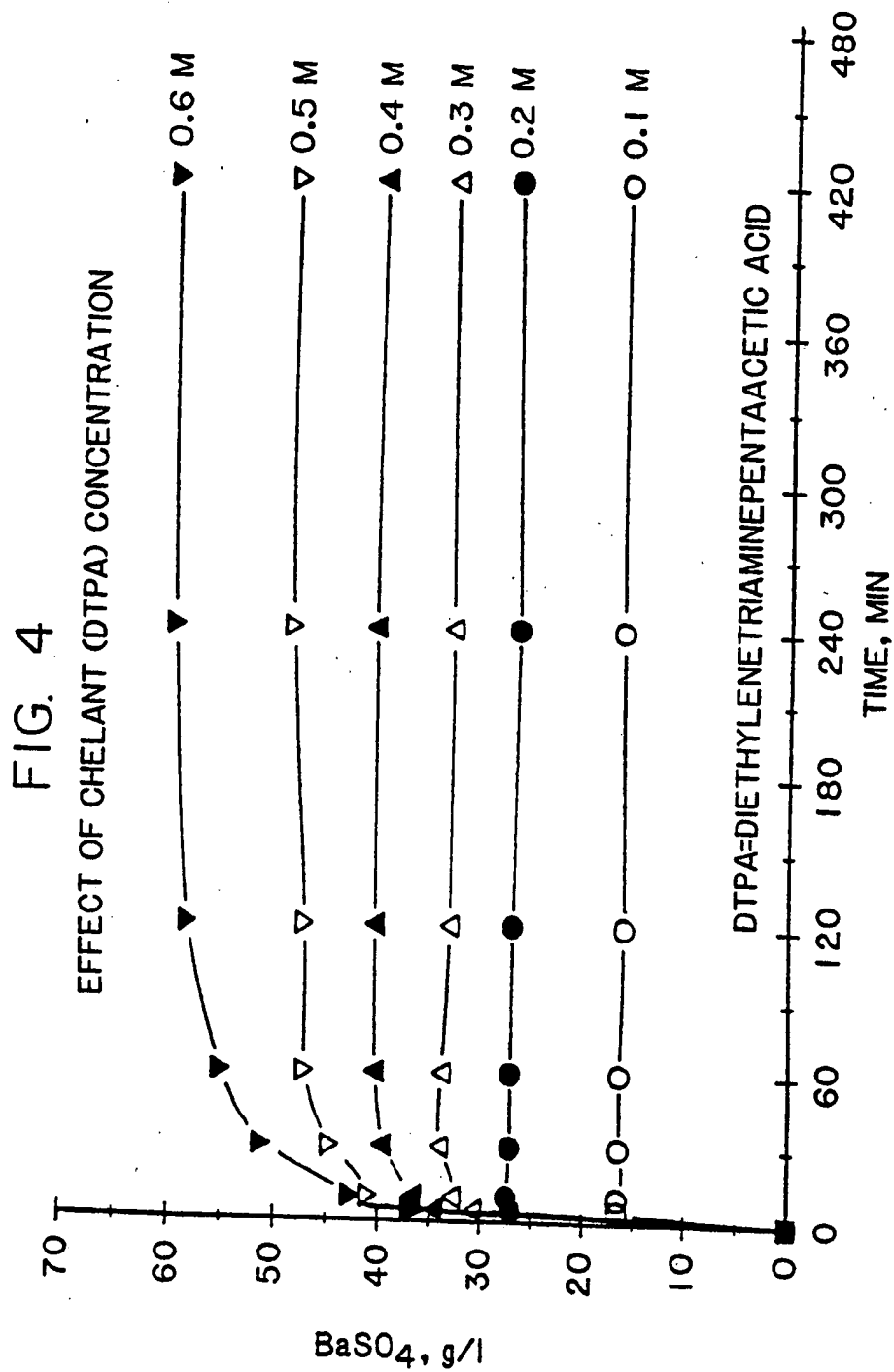
3/15

FIG. 3



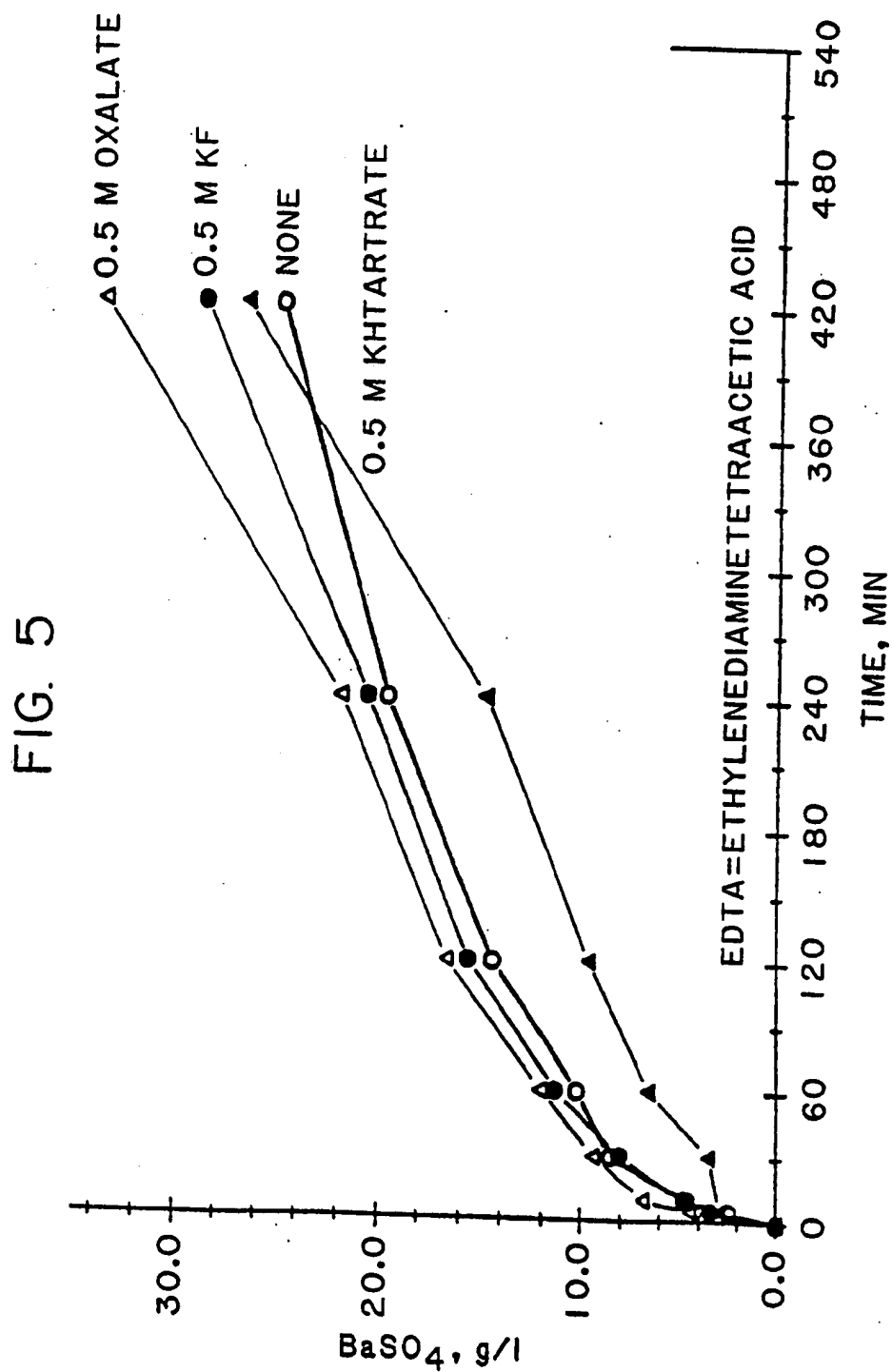
SUBSTITUTE SHEET

4/15



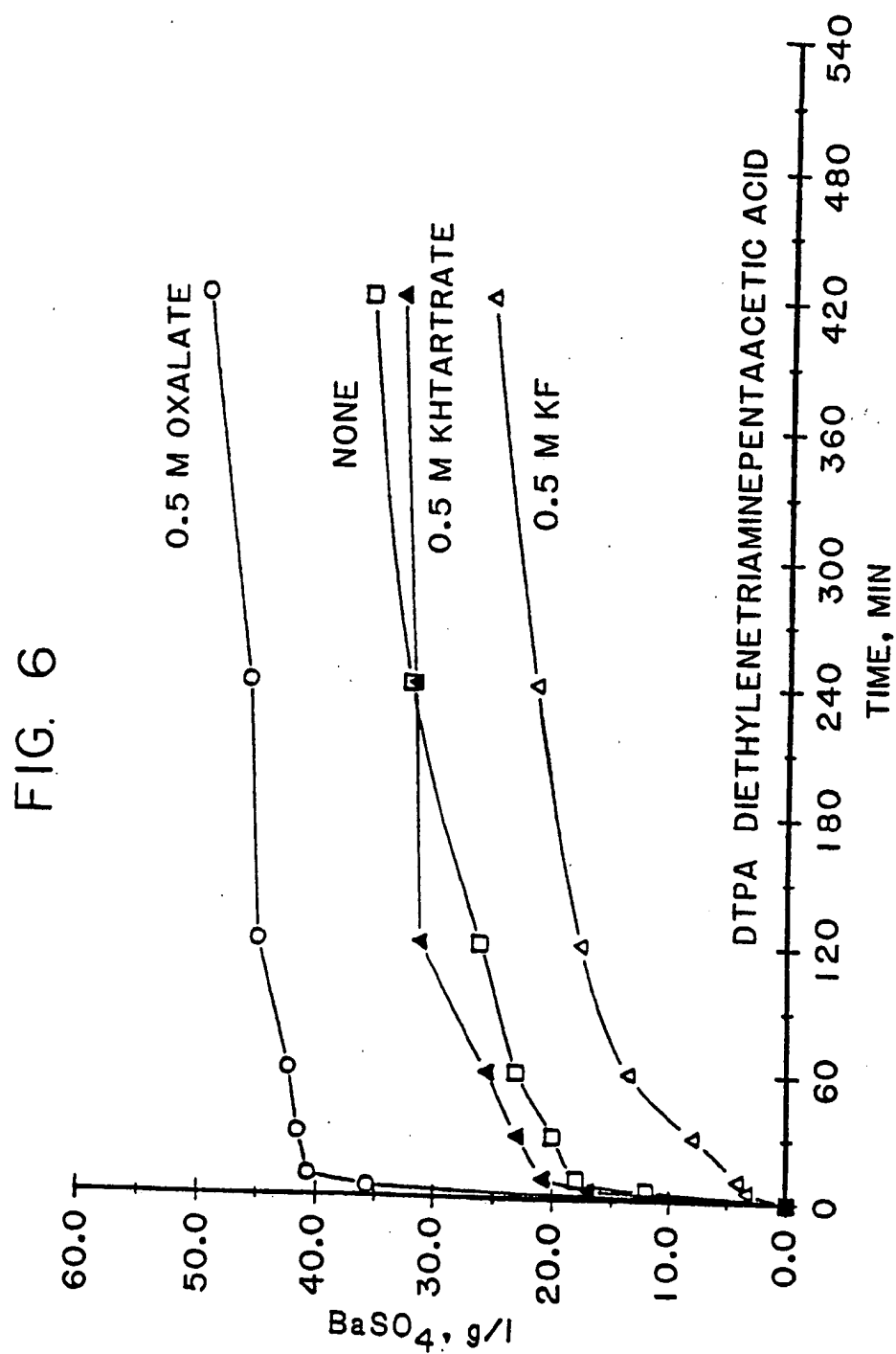
SUBSTITUTE SHEET

5/15



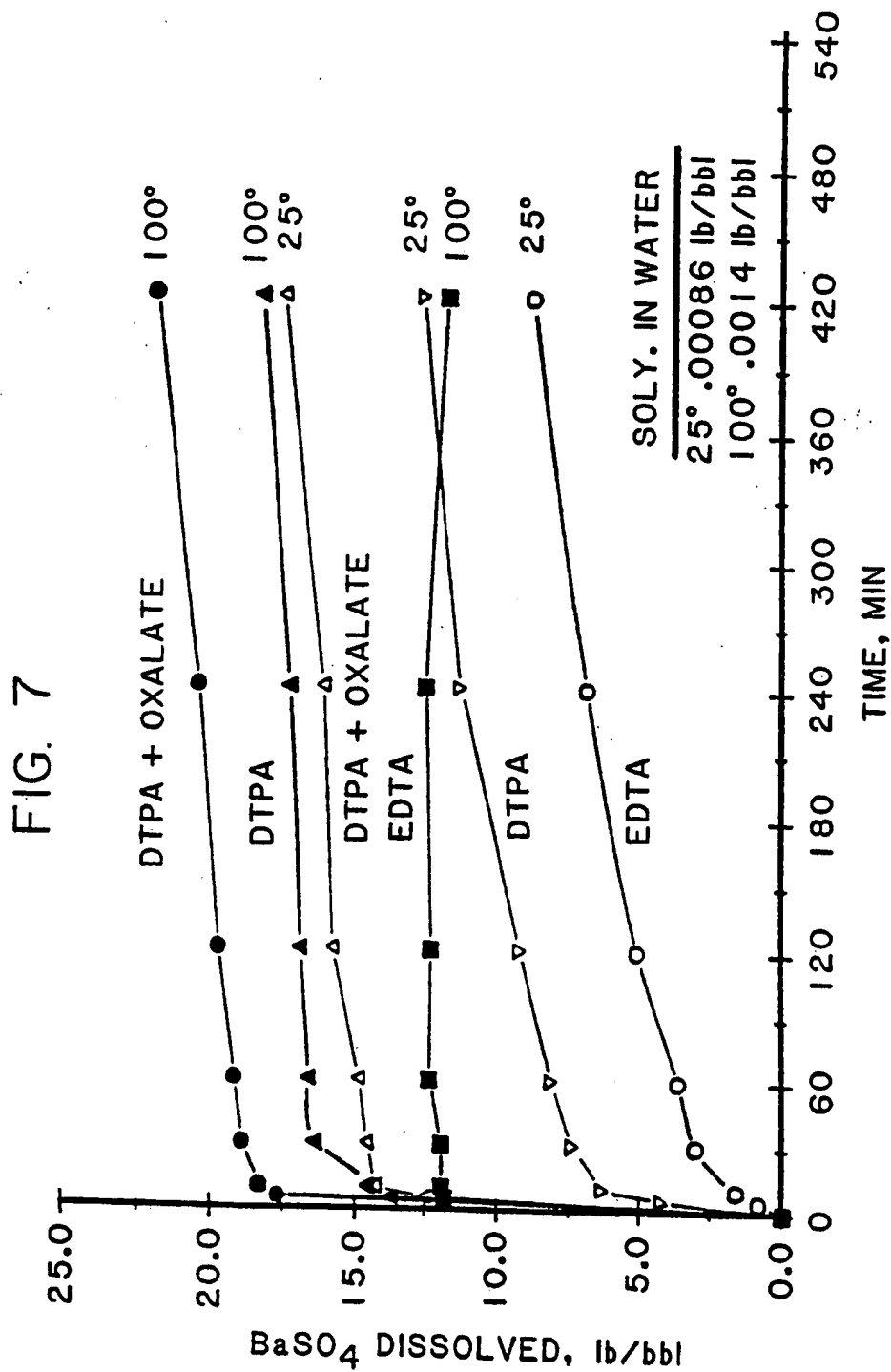
SUBSTITUTE SHEET

6 / 15



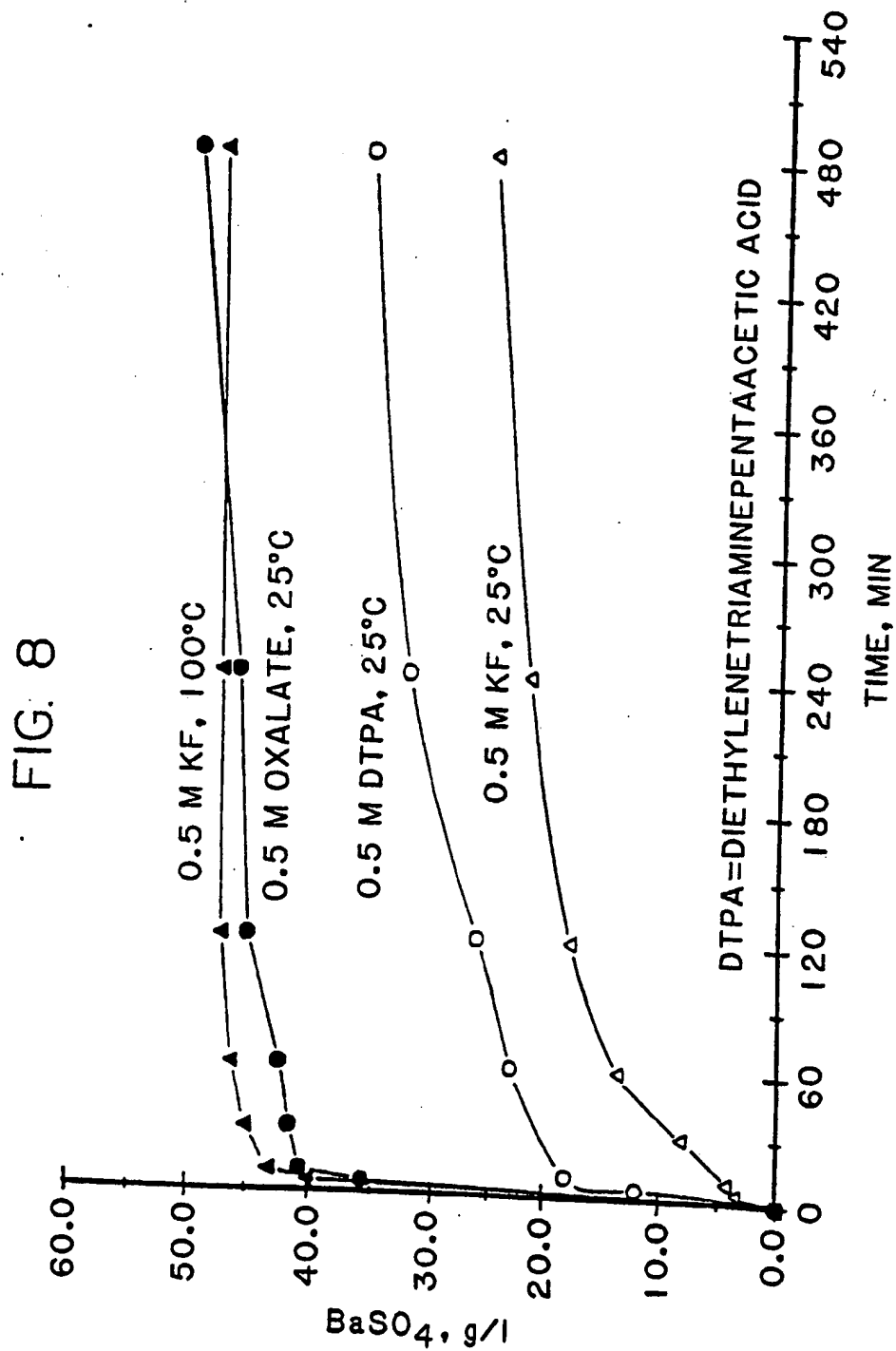
SUBSTITUTE SHEET

7/15



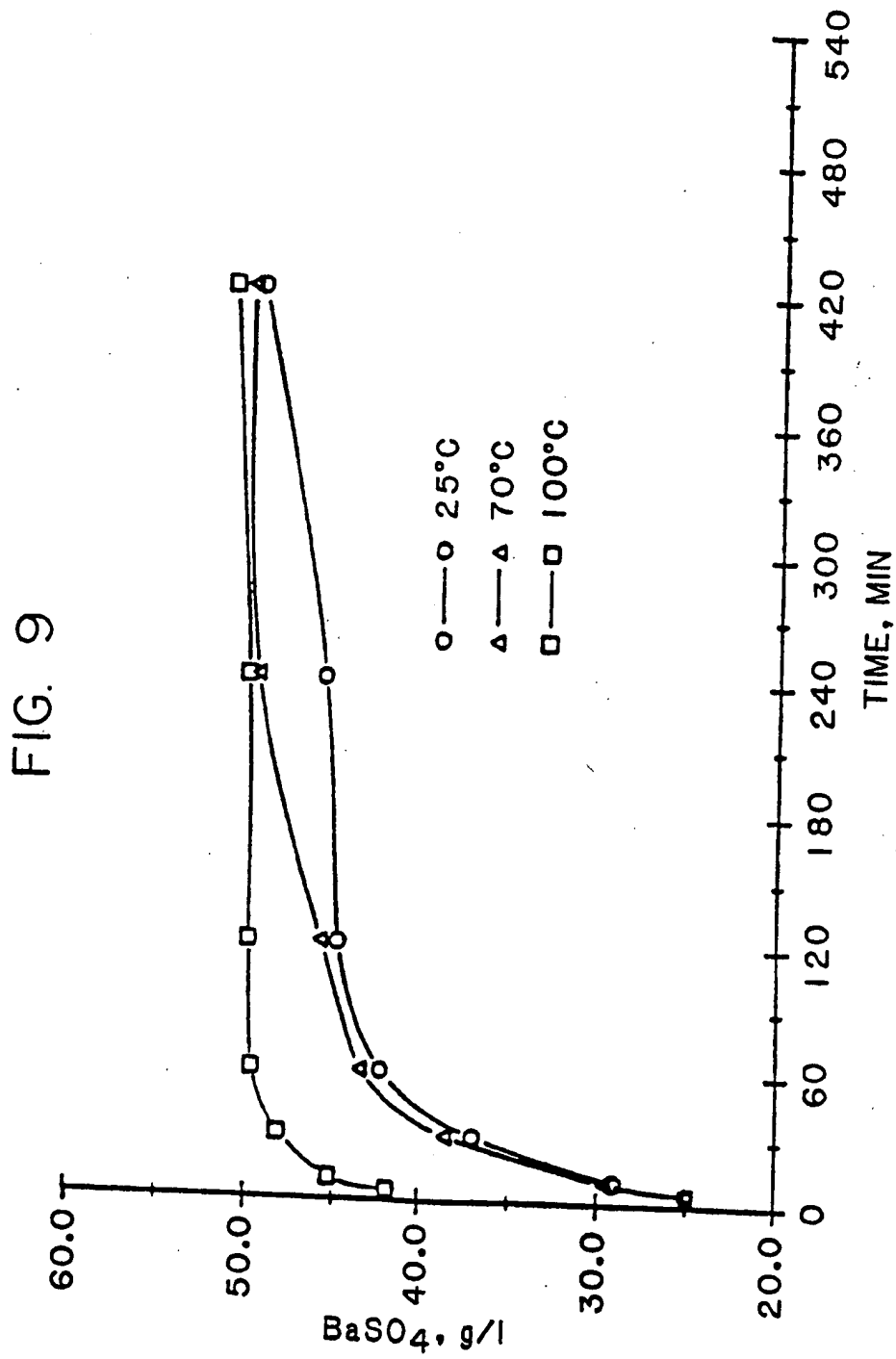
SUBSTITUTE SHEET

8 / 15



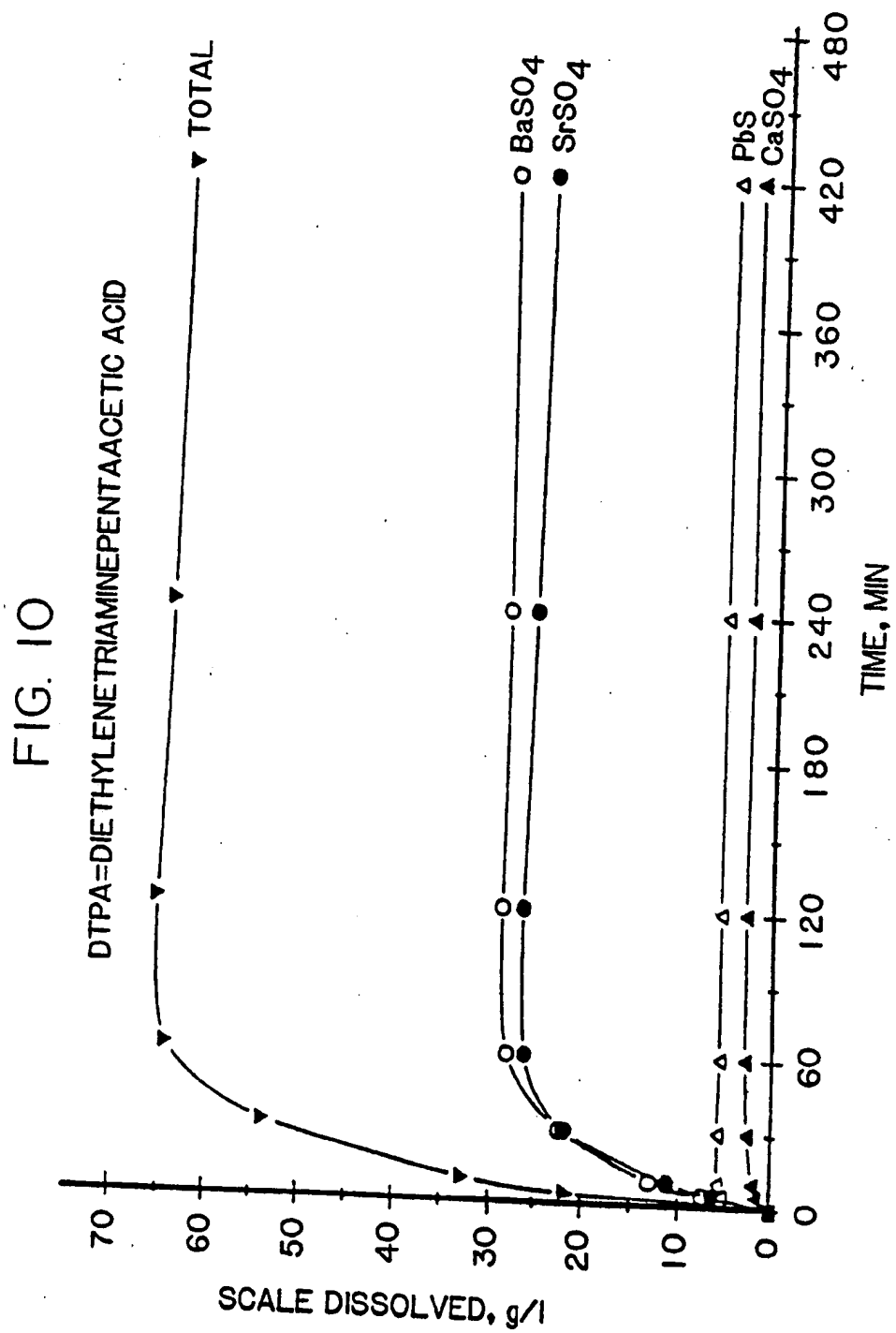
SUBSTITUTE SHEET

9/15



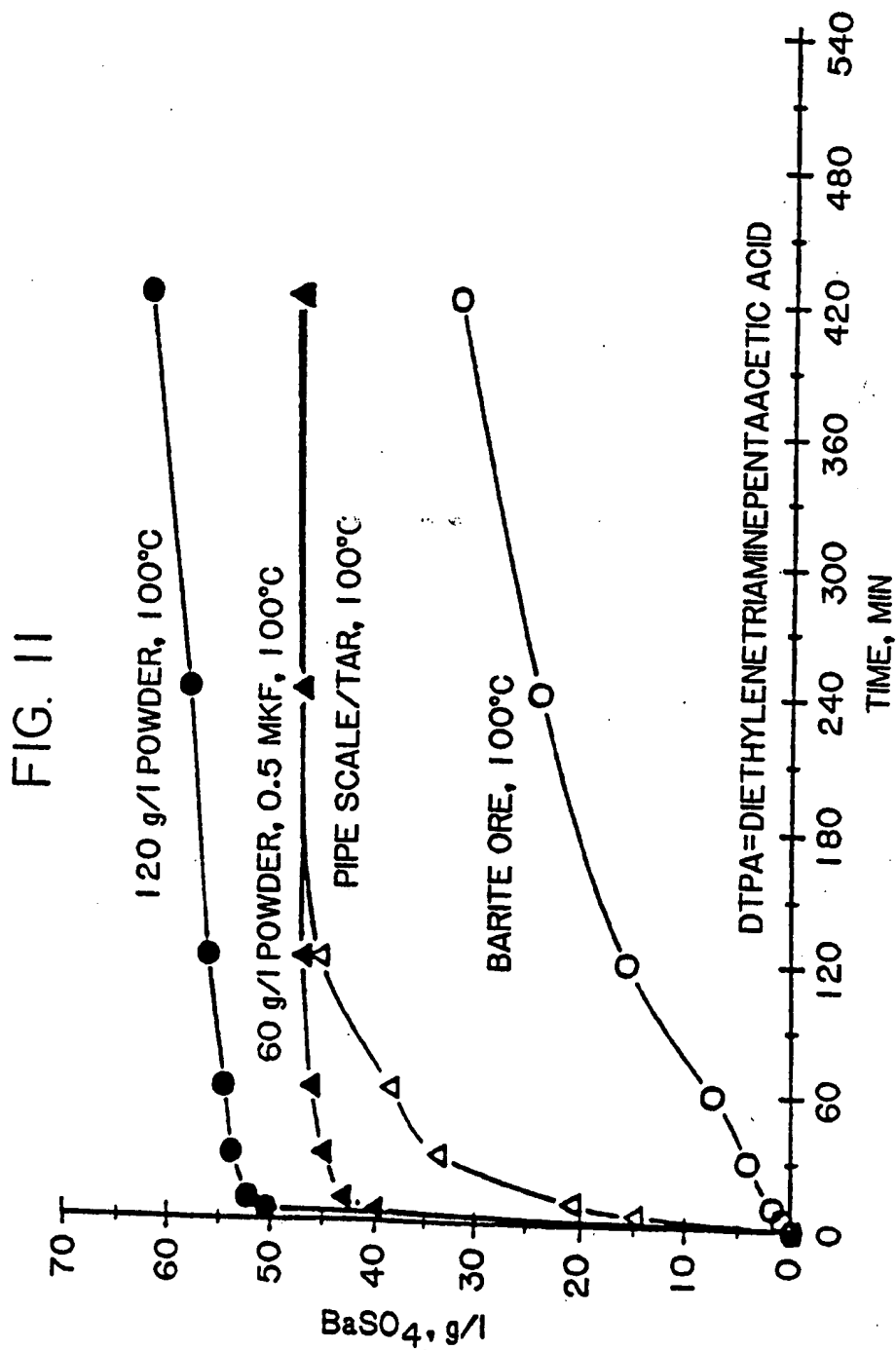
SUBSTITUTE SHEET

10/15



SUBSTITUTE SHEET

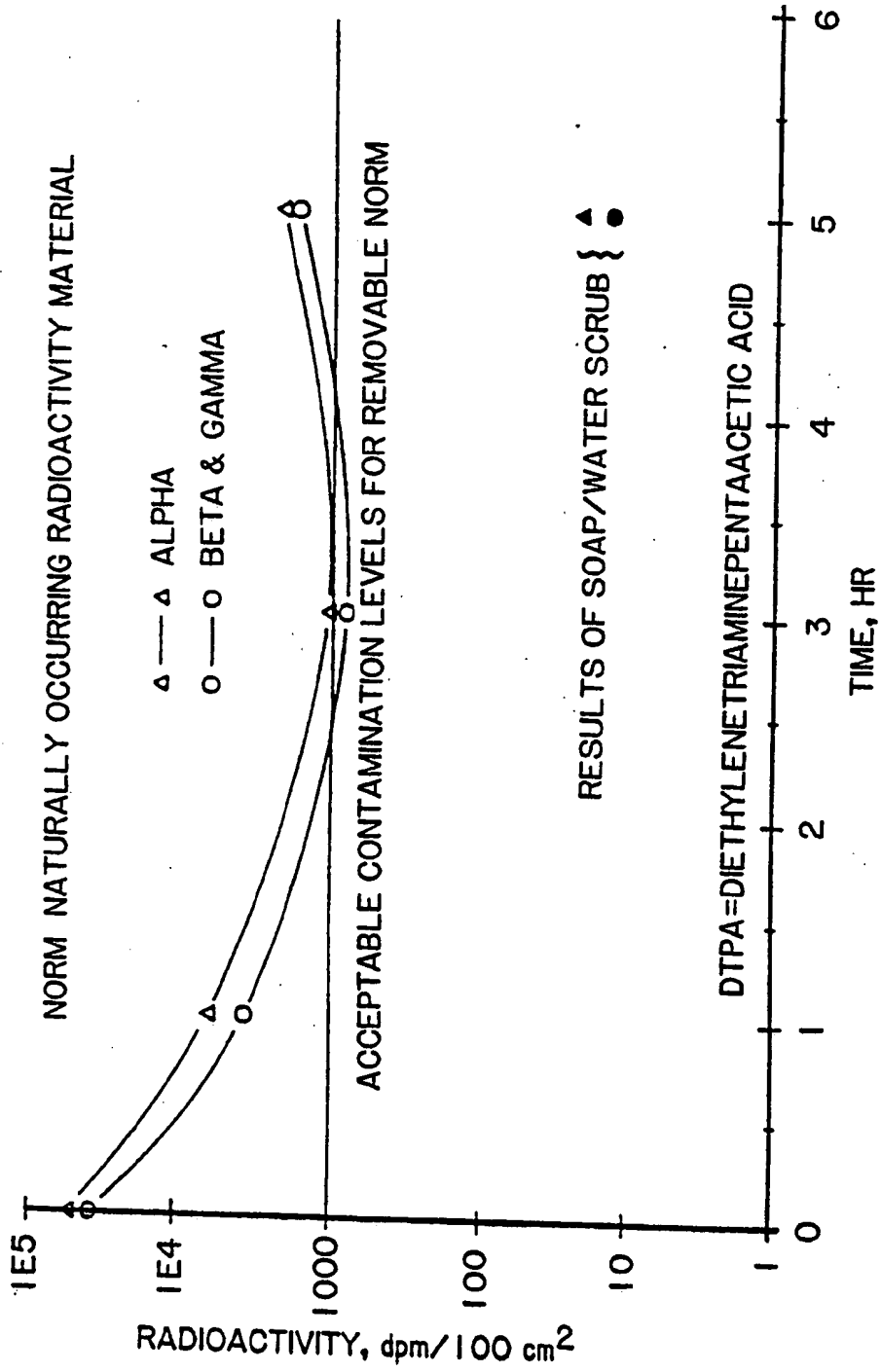
11/15



SUBSTITUTE SHEET

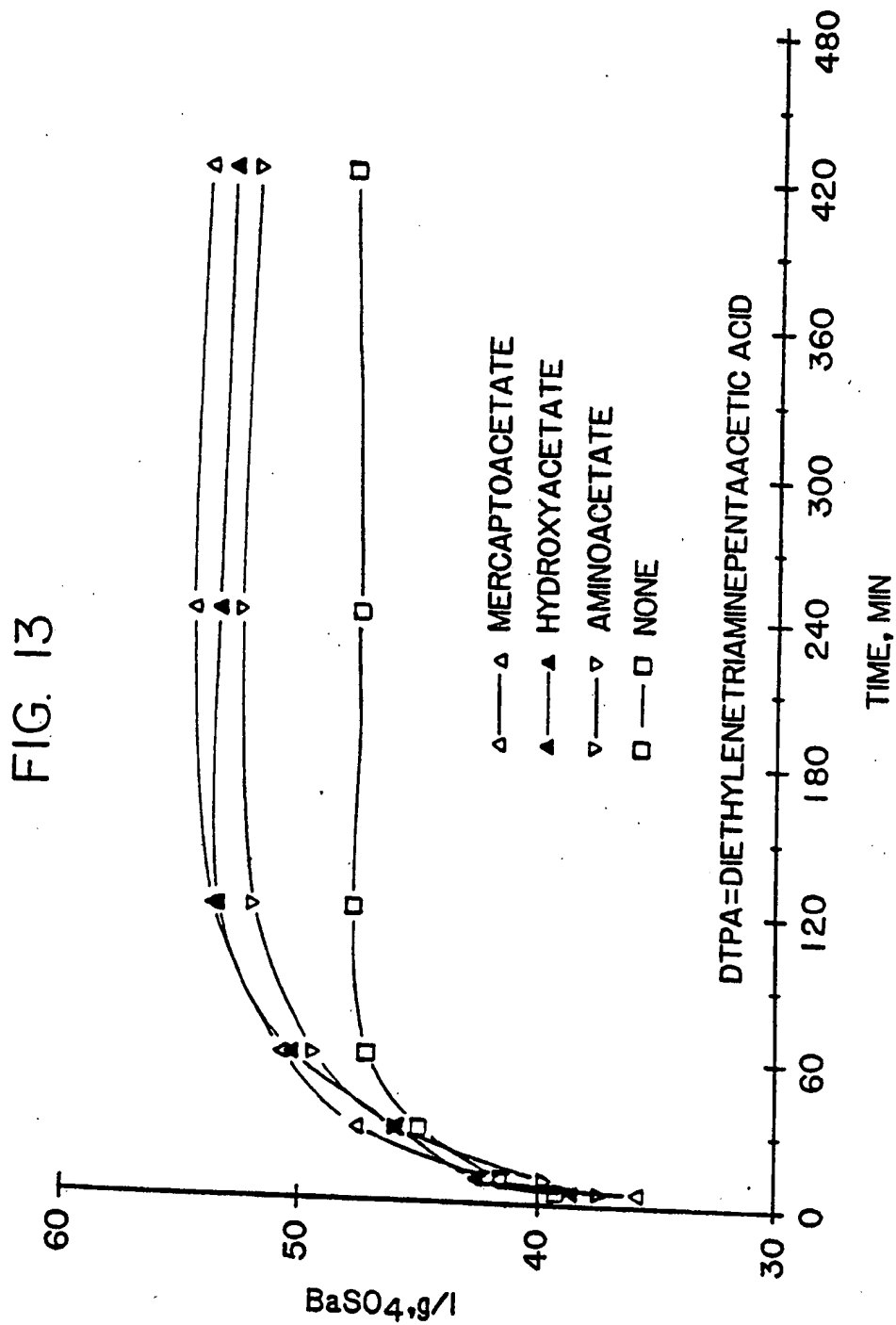
12 / 15

FIG. 12



SUBSTITUTE SHEET

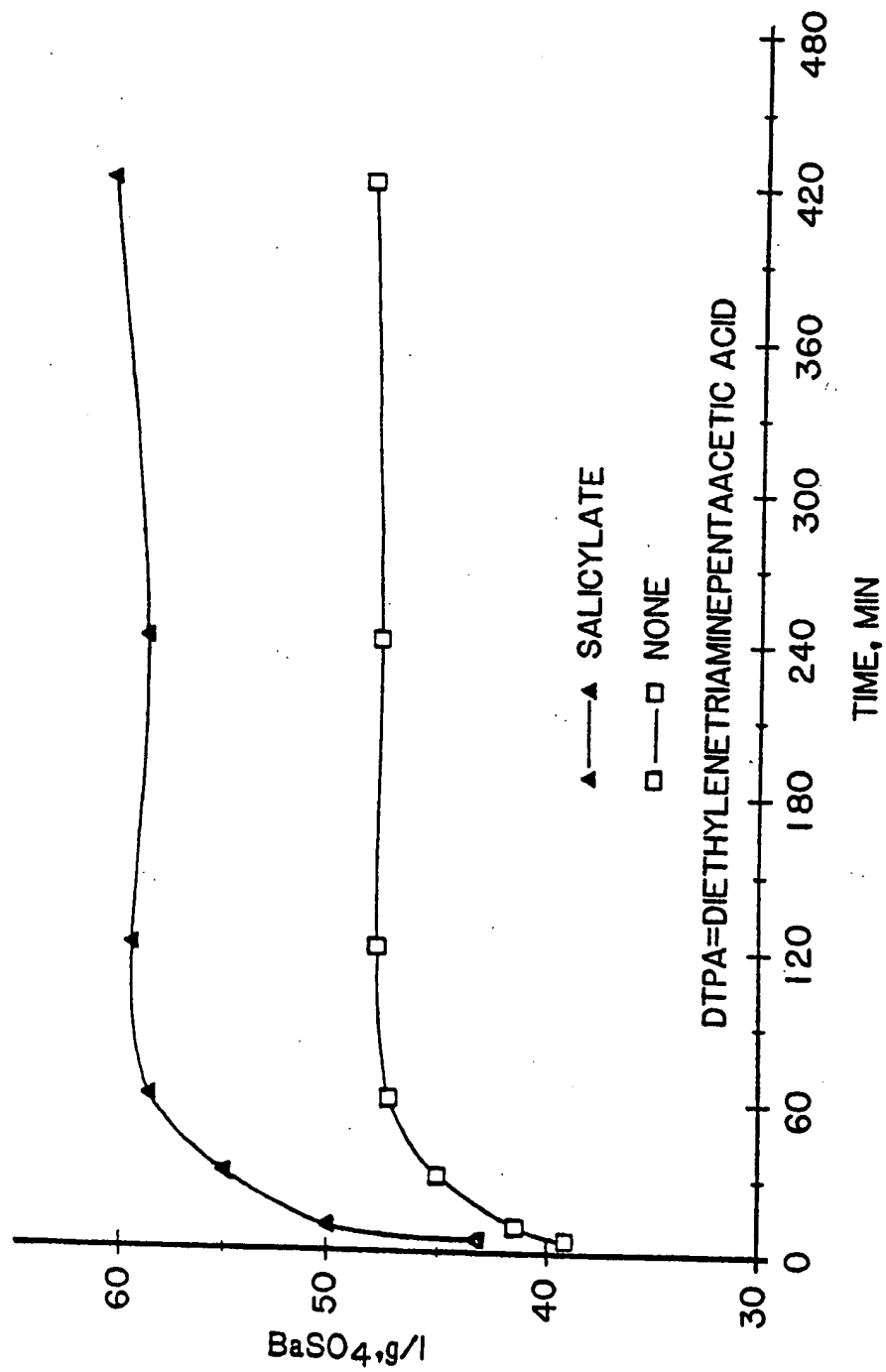
13/ 13



SUBSTITUTE SHEET

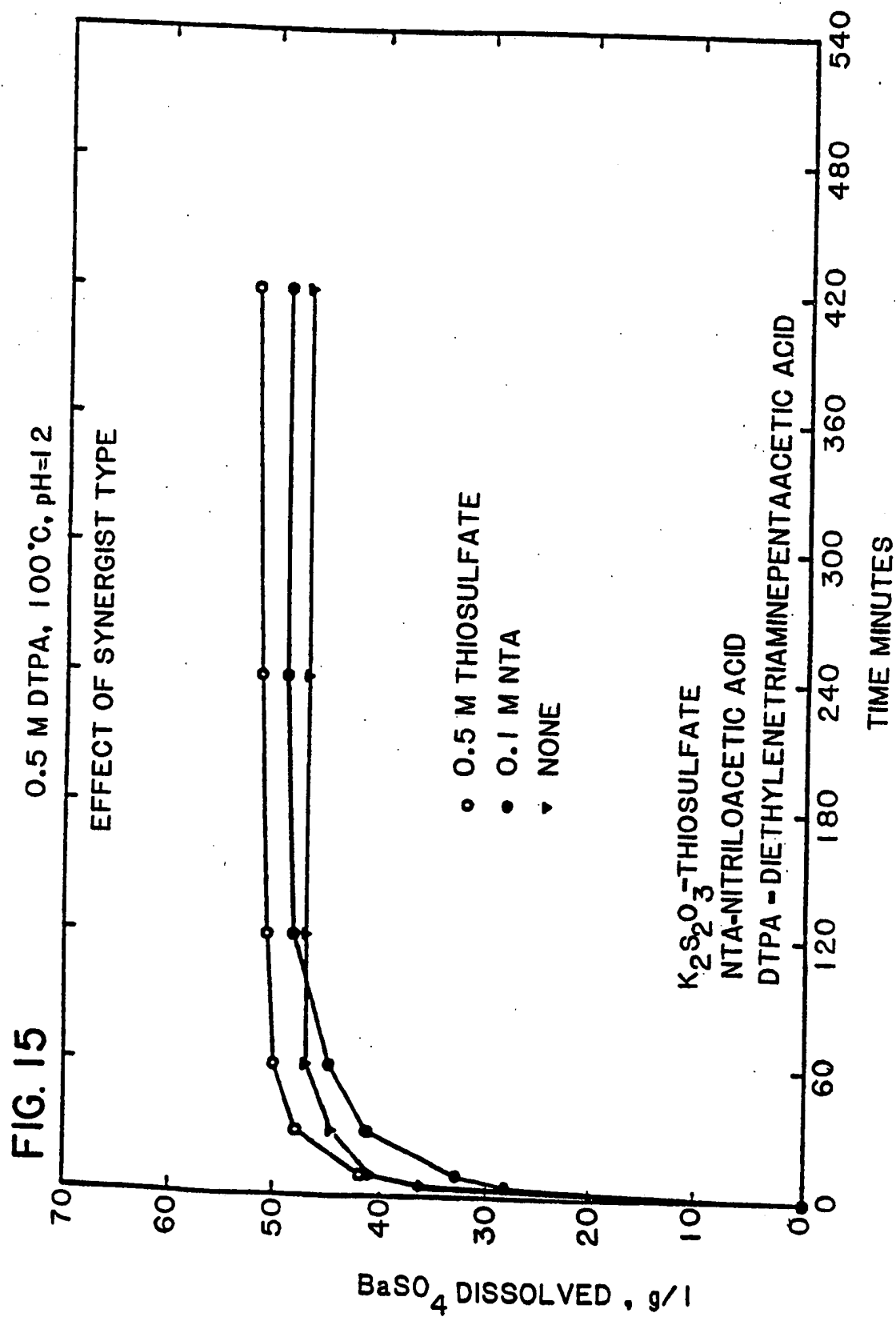
14/ 15

FIG. 14



SUBSTITUTE SHEET

15/15



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/01774

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 4

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC (5) C02 F 5/10; C23F 11/10; C23 G 1/06

US Cl. 252/80

II. FIELDS SEARCHED

| Minimum Documentation Searched 7 | |
|----------------------------------|-----------------------------------|
| Classification System | Classification Symbols |
| US | 252/80, 82, 175, 180 134/ 2, 3 |

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

| Category 9 | Citation of Document, 11 with indication, where appropriate, of the relevant passages 12 | Relevant to Claim No. 13 |
|------------|--|--------------------------|
| Y | US, A, 4,215,000, (De Jong et al) 29 July 1980 See column 4 line 15, column 5 line 68. | 1-50 |
| Y | US, A, 4,276,185 (Martin) 30 June 1981 See column 2 lines 14-57; Example 1. | 1-60 |
| Y | US, A, 4,708,805 (D'Muhala), 24 November 1987 See column 4 lines 1-20; column 7 lines 6-61 | 1-60 |
| Y | US, A, 3,625,761, (Tate), 23 December 1969 See column 2 lines 12-56; column 3 lines 43-60; column 4 lines 13-21. | 33-60 |
| A | US, A, 3,660,287, (Quattrini), 02 May 1972 See entire document. | 1-60 |
| A | US, A, 3,956,164 (Walker et al) 11 May 1976 See entire document | 1-65 |
| A | US, A, 4,030,548, (Richardson et al.) 21 June 1977 See entire document | 1-65 |

* Special categories of cited documents: 10

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step where the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

06 JUNE 1990

Date of Mailing of this International Search Report

01 AUG 1990

International Searching Authority

ISA/US

Signature of Authorized Officer

James M. Silbermann

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A

JP, A, 63-178199 (Hitachi Computer) 17 January 1987
See entire document

1-65

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.